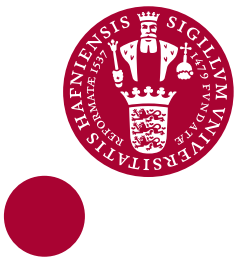

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Synthesis and electronic structure of heterometallic carbide-bridged complexes

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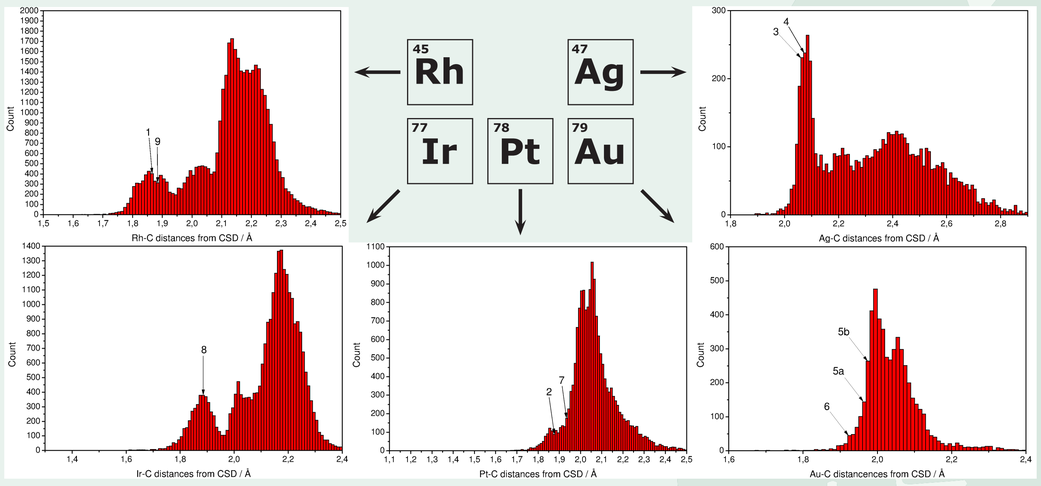
Introduction

Recently, it was reported that the FeMoco-cofactor of nitrogenase features a carbon-centered iron cluster[1,2]; consequently, we have embarked on the directed synthesis of carbide-bridged molecular systems. The terminal carbide complex $[Ru(C)Cl_2(Pcy_3)_2]$[3,4] is an excellent synthon due to its stability.[5] Previously, its coordination to palladium has been reported[4] with suggestion that the carbide moiety may function as a σ-donor. We report a series of novel carbide-bridged systems with low valent noble metals. The observed preference for coordination to low-valent centers and the concomitant short C-M bonds (see table and figure) suggest the ruthenium carbide to have pronounced π-acceptor capacity.

Synthesis and characterization

$[Ru(C)Cl_2(Pcy_3)_2]$ was dissolved in chloroform and allowed to react stoichiometrically with suitable low-valent metal complexes. ^{13}C-NMR is a powerful tool for examining the possibility of a successful synthesis prior to structure determination by X-ray diffraction owing to the bridging carbides' resonances which fall in the range 350-450 ppm (the chemical shift of the parent carbido complex is 471.66 ppm in $CDCl_3$). This renders the signal from the carbide bridge practically unmistakable.



Metal-carbide distances compared with the lengths of other metal-carbon bonds. The data are collected from a CSD search on the fourth of September 2012. The short metal-carbide distances are in concord with back-donation from the electron rich transition metals.

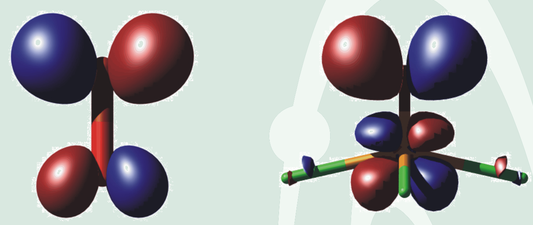


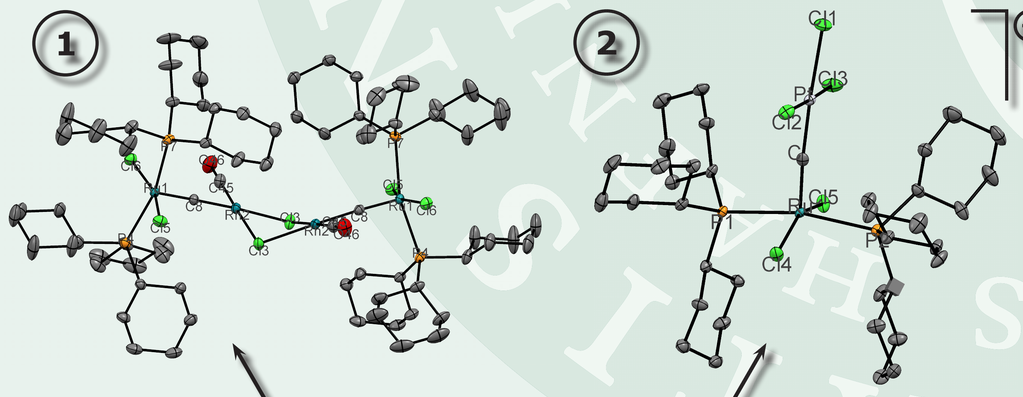
Illustration of the π-acceptor propensity of carbide complexes by comparison of LUMO's of CO (left) and $[Ru(C)Cl_4]^{2-}$ (right), respectively.

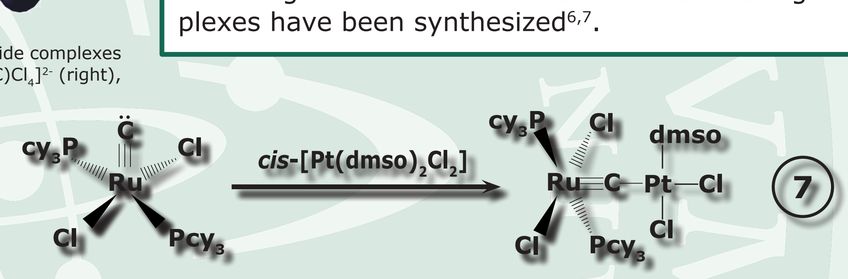
Similarities with nitrides

Formally, carbides and nitrides are derived from C^{4-} and N^{3-} ions. It has been shown computationally that the terminal carbide and nitride complexes function as strong π-acceptor ligands towards other metal centers; this is another resemblance between the carbides and the nitrides. Moreover, a series of analogous bimetallic nitride and carbide bridged complexes have been synthesized[6,7].

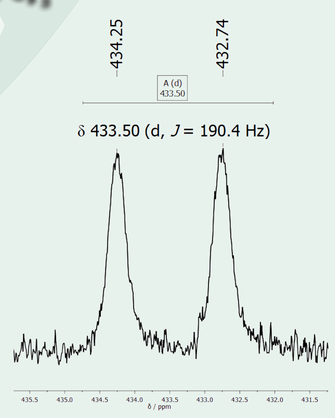
Metal-carbon metrics			
Complex	Ru-C / Å	C-M / Å	Ru-C-M / °
1	1.688(2)	1.864(2)	176.9(1)
2	1.693(6)	1.871(6)	174.6(3)
3	1.651(4)	2.072(4)	176.4(2)
4	1.642(3)	2.082(3)	177.2(2)
5a*	1.679(10)	1.960(10)	173.6(7)
5b*	1.655(9)	1.974(9)	175.4(7)
6	1.664(3)	1.921(3)	175.4(2)
7	1.666(5)	1.934(5)	177.7(4)
8	1.706(3)	1.886(3)	174.3(2)
9	1.699(9)	1.887(9)	173.3(5)

*5 crystallizes with two crystallographically independent but connectively identical molecules; this poster depicts 5a.





Other compounds synthesized and structurally characterized. The difference in reactivity between the rhodium compounds is pronounced since the dichloro bridge in $[Rh(cod)Cl]_2$ is cleaved symmetrically whereas $[Rh(CO)_2Cl]_2$ dissociates CO to form a tetranuclear structure.



^{13}C-NMR spectrum of $[(cy_3P)_2Cl_2RuC\text{-}Ag(terpy)]Otf$ showing the region where the carbide's signal is. The signal is split into a doublet since the abundance of naturally occurring silver nuclei with I = ½ is 100%.

Coupling constants	
Complex	$J_{C\text{-}M}$
1	59.6 Hz
2	1399.8 Hz
3	187.4 Hz
4	190.4 Hz
7	1347.3 Hz
9	59.4 Hz

Selected coupling constants from the compounds. All metal nuclei that give rise to a splitting of the carbide's signal have I = ½: naturally occurring Rh is composed exclusively of ^{103}Rh with I = ½, Ag is composed of 52% ^{107}Ag and 48% ^{109}Ag both of which have I = ½, and the portion of ^{195}Pt (I = ½) amounts to 34%.

Reactions with gold(I)

$[Ru(C)Cl_2(Pcy_3)_2]$ does not react with $AuClPph_3$, while treatment with $[AuPph_3]^+$ BF_4^- yields a trinuclear complex; moreover, the action of $AuCl(SC_4H_8)$ produces a dinuclear complex. Clearly, the chemistry of $[Ru(C)Cl_2(Pcy_3)_2]$ with various gold compounds may prove to be very rich.

Conclusion

The vast number of low valent transition metal complexes with the ruthenium carbide as ligand indicate its π-accepting nature; furthermore, the complexes represent an intriguing branch of molecular systems that may be used to elucidate the properties of the stealthy FeMoco-cofactor.

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